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Techniques for the Measurement of Aerosol Carbon Content

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TECHNIQUES FOR THE MEASUREMENT OF AEROSOL CARBON CONTENT

by

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EPA Grant No. 806005

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16. ABSTRACT

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An emission inventory for fine particle aerosol carbon has been constructed for the Metropolitan Los Angeles area and compared to the results of ambient sampling.

The relative contribution of primary and secondary carbon to urban aerosol has also been studied in this project.

The various portions of this work are published in the open literature as indicated in the text. This report is intended to serve as a guide to that literature.

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ABSTRACT

This report summarizes work on various aspects of measurement of carbon content of atmospheric aerosols carried out under EPA Grant No. R806005 to Washington University from June 1, 1978 through March 31, 1981. This work followed up a project begun under grant R803115 to Washington University from June 1, 1974 to May 31, 1978.

In this report we describe two different techniques for total and elemental carbon analysis which we have developed under this grant. Both methods are totally instrumental, automated, and non-destructive. Total carbon is determined using the gamma ray analysis of light elements (GRALE) technique. This method involves the in-beam measurement of γ rays emitted during the inelastic scattering of protons accelerated in a cyclotron. Elemental carbon is determined by a light reflectance method. Much of the analysis has been of aerosols deposited on low carbon glass and quartz filters. The extension of the method to teflon filters is also described.

An emission inventory for fine particle aerosol carbon has been constructed for the Metropolitan Los Angeles area and compared to the results of ambient sampling. Information on the level of source activity, total aerosol emission rate, particle size and chemical composition was used to estimate the mass emission rate of particulate organic and elemental carbon in this urban area.

The relative contribution of primary and secondary carbon to urban aerosol has also been studied in this project. Some data from the ACHEX study in Los Angeles have been reexamined using new values for carbon and lead emissions. Data on total carbon, elemental carbon and lead in fine particle samples collected in St. Louis were examined.

The various portions of this work are published in the open literature as indicated in the text. This report is intended to serve as a guide to that literature.

This report was submitted in fulfillment of Grant No. R806005 by Washington University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 1, 1978, to March 31, 1981, and work was completed as of May 31, 1981.

ACKNOWLEDGEMENTS

The input of coworkers Lih-Ching Chu, R. Delumyea and P. M. Boone of Washington University and Glen R. Cass and M. H. Conklin of Cal Tech are gratefully acknowledged. We are indebted to the Washington University Cyclotron staff for assistance in sample irradiation.

This work benefited in all phases from the very useful collaboration between Washington University researchers and EPA scientists at the Environmental Sciences Research Lab, Inorganic Pollutant Analysis Branch, particularly Project Officer Charles Lewis and Branch Chief Robert Stevens.

1. INTRODUCTION

Ambient aerosols, particularly those with diameters less than 3 μm are a serious pollution problem. Carbonaceous material is a major component of the fine particle concentration (Lewis and Macias, 1980) and has undergone extensive study in the past few years (Novakov, 1979; Wolff and Klimisch, 1981), in large part because of the concern that these particles play an important role in urban haze and community health.

Particulate carbon in the atmosphere exists predominantly in three forms: elemental carbon (soot) with attached hydrocarbons; organic compounds; and carbonates. Carbonaceous urban fine particles are composed mainly of elemental and organic carbon. These particles can be emitted into the air directly in the particulate state or condense rapidly after introduction into the atmosphere from an emission source (primary aerosol). Alternatively, they can be formed in the atmosphere by chemical reactions involving gaseous pollutant precursors (secondary aerosol). The rates of formation of secondary carbonaceous aerosol and the details of the formation mechanisms are not well understood. However, an even more fundamental controversy exists regarding the relative amounts of primary and secondary carbonaceous aerosols in urban air.

A number of techniques for carbon analysis based on combustion and optical attenuation (Huntzicker et al., 1980; Stevens et al., 1980; and Gerber et al., 1980) have been developed. In this report we describe two different techniques for total and elemental carbon analysis which we have developed under this grant. Both methods are totally instrumental, automated, and nondestructive. Total carbon is determined using the gamma ray analysis of light elements (GRALE) technique (Macias et al., 1978; Macias et al., 1979). This method involves the in-beam measurement of γ rays emitted during the inelastic scattering of protons accelerated in a cyclotron. Elemental carbon is determined by a light reflectance method (Delumyea et al., 1980). Much of the analysis has been of aerosols deposited on low carbon glass and quartz filters. The extension of the method to teflon filters is also described (Chu et al., 1980).

These methods have been used extensively for studies in Charleston, WV (Lewis and Macias, 1980), St. Louis, MO (Macias et al., 1979; Chu and Macias, 1980), the southwestern US (Macias et al., 1980), Los Angeles, CA (Cass et al., 1981; Conklin et al., 1980) and China Lake, CA (Ouimette, 1980).

2. EXPERIMENTAL PROCEDURES

TOTAL CARBON ANALYSIS BY THE GRALE TECHNIQUE

The total carbon content of the aerosol samples has been determined using the gamma-ray analysis of light elements (GRALE) technique (Macias et al., 1978). This non-destructive technique is based on the measurement of gamma-ray emission induced by proton bombardment of aerosol samples. The gamma-ray energy is, in general, unique to a particular nuclide and thus can be used as a signature for the element. Elemental concentrations are obtained in units of $\mu g\ cm^{-2}$ and are not affected by the chemical form of the elements. The GRALE technique has been used for total carbon analysis but the method can also be used for determining the concentration of other elements such as sulfur, nitrogen, and oxygen.

Following collection, the filter samples are mounted in 5 x 5 cm slide mounts after removal of the cellulose backing. The samples are then irradiated with a collimated beam of 7 MeV protons in the external beam facility of the Washington University 135-cm sector focused cyclotron with an automated sample changing chamber maintained in 1 atm of helium. The experimental setup is shown schematically in Figure 1.

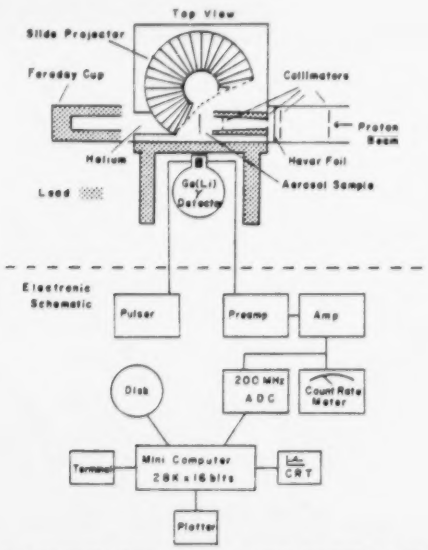


Figure 1. Schematic diagram of the sample irradiation chamber and electronics used for carbon analysis by the GRALE technique.

Gamma rays produced in the proton bombardment are detected with a 60-cm^3 lithium drifted germanium Ge(Li) detector (11.7% efficient relative to a 7.5 x 7.5 cm NaI(Tl) detector of 1332 keV gamma rays), with energy resolution of 2.5 keV full width at half maximum for 1332 keV gamma rays. The gamma ray data are stored and processed in a PDP-11 mini-computer with a 28000 word memory (Digital Equipment). The spectra are analysed immediately after each irradiation with the on-line computer. The intensity of each peak is determined from the integrated peak area after subtraction of background. The peak intensity is corrected for system dead time losses (typically 20%) determined from the area of a pulser peak in the spectrum produced from a 60 Hz tail-pulse generator. These data are normalized to the proton beam intensity and intensities of the filter blanks are subtracted from the aerosol results.

TOTAL CARBON CALIBRATION

Carbon peak intensity is converted into carbon mass by calibrating with standard methionine aerosol ($C_5H_{11}O_2SN$) deposited on the same type of filter. The mass of methionine deposited on the filter is determined using a beta attenuation mass monitor. Filter blanks, atmospheric, laboratory and methionine standard aerosol samples are run under nearly identical conditions which yield nearly equal detector count rates. All samples are analyzed in the same way.

METHOD INTERCOMPARISON

The GRALE technique has been extensively compared to other techniques (Macias et al., 1978). In that work the total carbon analysis of the same or duplicate filters was carried out with the GRALE method, the Dohrmann DC-50 carbon analyser (Envirotech) and the Perkin-Elmer Model 240 Elemental Analyser (Perkin-Elmer) as shown in Figure 2. The latter two methods are based on

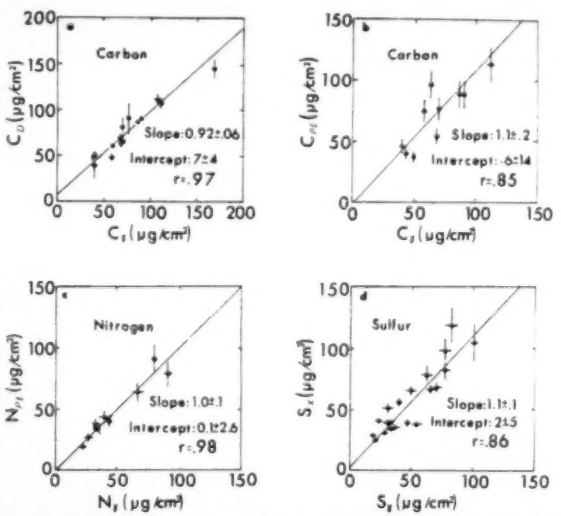


Figure 2. Method intercomparison of atmospheric fine particle samples. In each plot the results of the γ-ray method is the abscissa. The ordinate is the result of the Dohrmann device in frame a, the Perkin-Elmer device in frames b and c, and x-ray fluorescence in frame d. The line in each plot is the linear least squares fit to the data

the high temperature combustion of carbon compounds with subsequent detection of CH_4 and CO_2, respectively. This intercomparison indicated that to within 5% there are not systematic discrepancies in any of the methods investigated. The advantages of the GRALE technique over combustion methods are that it is non-destructive and unaffected by the chemical form of the aerosol.

ELEMENTAL CARBON ANALYSIS BY REFLECTANCE

A laboratory reflectometer, shown schematically in Figure 3 has been constructed for use with fine particle filter samples. This light-tight

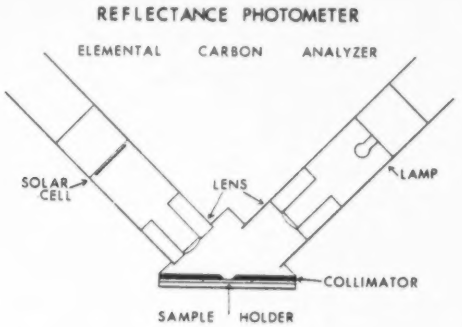


Figure 3. Reflectance Photometer.

system consists of two blackened aluminum tubes (5.5-cm dia.) each mounted at 45° to an aluminum sample chamber which holds standard 5 x 5 cm slide mounts. A 12-V tungsten filament lamp powered by a stabilized 12-V supply is used as a light source. Plano-convex lenses (2.3-cm dia., 4.5-cm focal length) are used to focus the incident light onto the sample (0.3 cm^2) and reflected light onto a solid state photodetector (N/P silicon solar cell, Centerlab Semiconductor, Inc.). The intensity of the solar cell output is monitored with a digital voltmeter. Unexposed filter, taken from the same filter roll as the samples, is used to determine the initial, or blank, intensity (I_o). Blank values are obtained after the intensity of each sample is determined in order to minimize the effect of any drifts in the electronics.

PREPARATION OF ELEMENTAL CARBON STANDARDS

Aerosol particles of elemental carbon (as soot) were prepared by the combustion of polystyrene, paraffin and butane. The aerosol generated was aspirated into a 5 ℓ container, mixed with filtered air and drawn through a sampler equipped with the on-line reflectometer. The mass of the deposit was determined by beta attenuation (Macias and Husar, 1976A). The reflectance of the spot before and after loading was also measured. Since the aerosol could contain appreciable non-elemental carbon (organic) compounds a method for their removal was developed. A set of butane-generated samples was mounted over a 1.3 cm dia. hole in 5 x 5 cm aluminum plates and total carbon deter-

mined via the GRALE technique. The samples were then placed in the oven of a conventional gas chromatograph equipped with a programmable temperature ramp. Samples were heated at 20° C min^{-1} to a fixed temperature and left at that temperature for 20 min. The reflectance of the sample was measured after cooling to room temperature, then the procedure was repeated at a higher temperature. The reflectance of the sample was nearly constant up to 350° C. Above 350° C the reflectance relative to 25° C increased, indicating loss of elemental carbon. Therefore a temperature of 300° C was used to remove organic compounds from the soot samples with minimal loss of elemental carbon.

Analysis of butane-generated samples for total carbon content by GRALE after heating to 300° shows ∿25% carbon loss upon heating without appreciable change in reflectance. The after-heating GRALE carbon mass was taken to be the actual elemental carbon content of the samples which were then considered elemental carbon standards.

A calibration curve, shown in Figure 4 was prepared by plotting the log

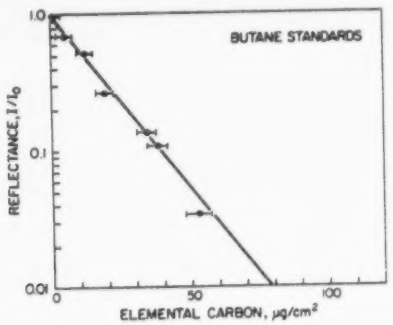


Figure 4. Calibration curve determined from elemental carbon standards. The log ratio of reflectance is plotted on the ordinate. The elemental carbon mass determined by GRALE analysis after heating to 300°C is plotted on the abscissa.

of the ratio of the final to initial reflectance of the elemental carbon standards versus the carbon mass determined by GRALE analysis after heating to 300° C. Alternately the total mass of the soot standard after heating to 300° C determined by beta attenuation can be used in place of the GRALE carbon mass.

3. MEASUREMENTS WITH ATMOSPHERIC SAMPLES

Atmospheric fine particle aerosol samples were collected on the roof of the six story Chemistry building of Washington University, located 6 miles west of downtown St. Louis. The immediate area is primarily residential with a major expressway one mile away which is usually upwind from the sampling site. Samples were collected on an automated TWOMASS sampler equipped with the on-line reflectometer and β-attenuation system (Macias and Husar, 1976B) for soot carbon and mass analysis. The samples were analyzed via the GRALE technique for total carbon content. Samples were then heated and the carbon content and reflectance remeasured after heating. Figure 5 shows the

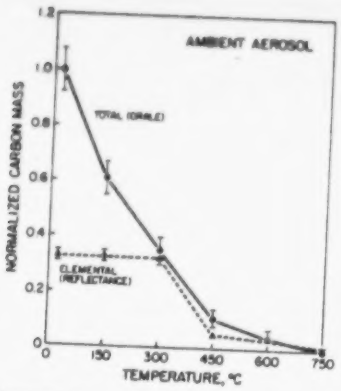


Figure 5. Average decrease in total and elemental carbon in atmospheric aerosol samples with increasing temperature.

average decrease in total and elemental carbon content with temperature of two samples collected on pre-ashed Pallflex Tissue Quartz (2500 QAO) filters. It can be seen that a significant amount of carbon is lost at temperatures up to 300° C without an appreciable loss of elemental carbon. We assume that this carbon loss at or below 300° is due to volatile organic compounds. However we cannot be certain that all organic compounds have been removed at this temperature. The amount of organic carbon loss below 300° C is dependent on the composition of the aerosol. Between 300 and 450° C, the carbon content continues to decrease with a corresponding decrease in reflectance due primarily to the loss of elemental carbon.

It is instructive to compare the amount of total and elemental carbon determined after heating atmospheric aerosol samples to 300° C in order to estimate the amount of non-elemental carbon remaining at that temperature. This comparison is shown in Figure 6 for 6 ambient samples. The data show a

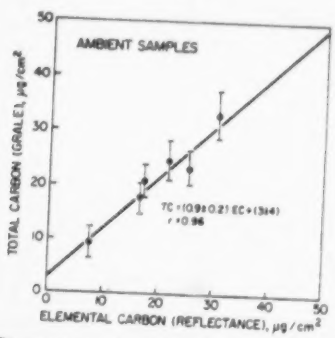


Figure 6. Comparison of total and elemental carbon determined after heating atmospheric aerosol samples to 300°C. The solid line is the least squares fit to the data.

high correlation (r = 0.96) indicating a linear relationship between elemental carbon and total mass. The least squares fit to the data has a slope near

unity (slope = 0.9 ± 0.2) indicating good agreement between total and elemental carbon. The $\underline{y}$ intercept is 3 ± 4 μg cm^{-2} which indicates there may be a small acount of non-elemental carbon remaining at 300° C in these ambient samples.

4. TOTAL AND ELEMENTAL CARBON ANALYSIS ON TEFLON FILTERS

The work described above employed glass or quartz filters. Teflon filters present a different problem because this material is 24% carbon [$(C_2F_4)n$]. Previously no carbon analysis method has been shown to be applicable with this high carbon filter. However, if the carbon to fluorine mass ratio is constant in teflon filters, the fluorine γ-ray can be used as an internal standard in GRALE analysis to indicate the thickness of the filter blanks and to determine the carbon filter blank value. In this section we describe the successful extension of the GRALE and reflectance analysis techniques for total and elemental carbon for use with teflon filters.

Teflon filters with 1 μm pore size and a nominal areal density of 1 mg/cm^2 mounted on a 37 mm polyolefin ring (Ghia Corp. Pleasanton, CA) and Pallflex E-70 glass fiber filter tape with a detachable cellulose backing (Pallflex, Inc. Putnam, CT) were used as filter media.

Ambient aerosols were collected with a manual dichotomous virtual impactor sampler (Dzubay et al., 1977) and a TWOMASS automated sequential tape sampler from the same aerosol manifold simultaneously. Both samplers fractionated the aerosol into two size classes; the fine fraction consisting of particles with aerodynamic diameters less than 3 μm were examined in this study.

The dichotomous sampler employed teflon filters; the TWOMASS sampler used glass fiber as a filter medium. Six, 12 and 24 hr samples were collected using the dichotomous sampler operated at a flow rate of 14 ℓ/min. Six hr samples were collected with the TWOMASS sampler at a flow rate of 12 ℓ/min. Both samplers were equipped with automatic flow controllers; the flow was also monitored manually.

Standards for total and elemental carbon analyses on teflon filters were prepared with methionine and butane soot aerosols as described previously. GRALE analysis of blank teflon filters yielded a linear relationship between fluorine counts and carbon counts ($r = 0.99$), as shown in Figure 7. This indicates that fluorine can be used for subtraction of carbon background from teflon filters. Teflon blanks gave a C/F count ratio of 0.128 ± 0.004. The large variation in carbon counts on blank filters shows that a reliable calibration can be achieved only when a correction for variations in carbon of the teflon filters is made by using the fluorine peak intensity as an indicator.

The average intensity of the 1.35 MeV fluorine peak from the blank filters was chosen as the standard reference peak for fluorine. The 4.43 MeV carbon peak intensity associated only with the deposited carbon was obtained using the following equation:

$$C_D = [C_S - (\overline{C/F})_B F_S] * N_{Beam}$$

where C_D is the carbon intensity from the deposit, C_S is the total carbon intensity from the sample, $(\overline{C/F})_B$ is the average C/F ratio for blank filters, F_S is the total fluorine intensity from the sample and N_{Beam} is a normalization factor which corrects for variations in the proton beam.

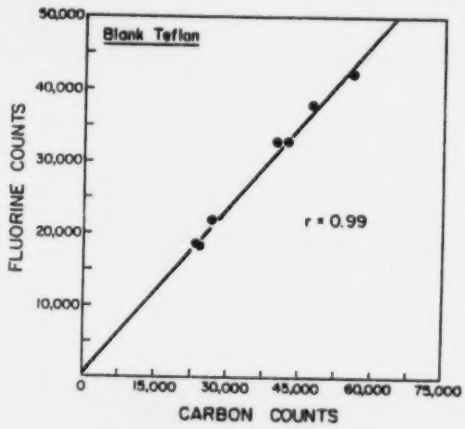
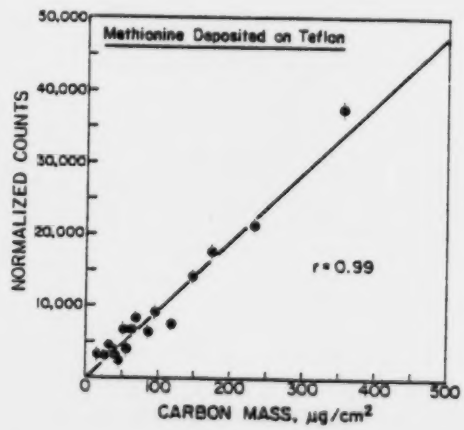


Figure 7. Correlation between fluorine counts and carbon counts from GRALE analysis for blank teflon filters.

Using this method, a calibration curve for carbon obtained from methionine standards was constructed as shown in Figure 8a. As seen in this figure, the proportionality between the measured γ-ray counts and deposited carbon is excellent (r = 0.99).



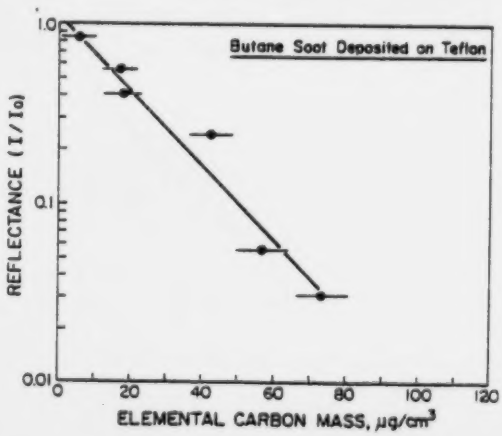


Figure 8a. Calibration curves for total carbon analysis of methionine aerosols collected on teflon filters by GRALE.

Figure 8b. Calibration of the laboratory reflectance photometer for carbon generated from a butane flame collected on teflon filters.

A typical calibration curve for elemental carbon, using butane soot deposited on teflon filters is shown in Figure 8b. This curve was prepared by plotting the log of the ratio of reflectance of the blank filter (I_o) to the reflectance after addition of the soot (I) versus carbon mass determined by the GRALE technique. The deposited soot mass on these calibration samples was also determined gravimetrically. The comparison of these two methods of calibration is shown in Figure 9. The linear correlation between the results of

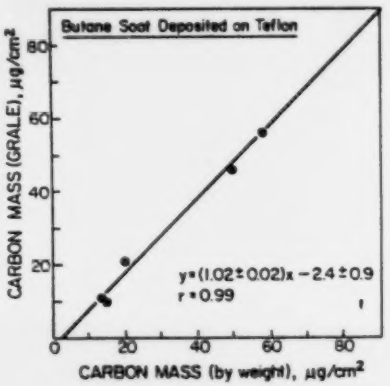


Figure 9. Comparison of elemental carbon analysis by reflectance using soot standard masses determined gravimetrically and by GRALE.

two methods is excellent. The slope is 1.02 ± 0.02 and the correlation coefficient is 0.99. The negative intercept indicates that there is a very small amount of impurity in carbon soots which contribute to the weight determined gravimetrically but is not measured as elemental carbon by GRALE.

The total carbon detection limit is estimated from the irradiation conditions and counting statistics. The minimum sensitivity (1σ) with teflon filters is 10 $\mu g/cm^2$ which corresponds to 1.5 $\mu g/m^3$ for 6 hr sampling at 14 ℓ/min with a 10 mm diameter sample deposit. This compares to 4.5 $\mu g/cm^2$ on glass fiber filters or 0.7 $\mu g/m^3$ for 6 hr sampling under the same conditions as above.

The reflectance analysis of elemental carbon on teflon filters has a minimum detectable limit of 1.8 $\mu g/cm^2$ or 0.3 $\mu g/m^3$ for 6 hr sampling as given above. The upper detection limit of the reflectance method due to saturation of the surface is $\sim$70 $\mu g/cm^2$.

5. COMPARISON OF CARBON ANALYSIS ON TEFLON AND GLASS FIBER FILTERS

Fine ambient aerosols were collected on both teflon and glass fiber filters during the period of February 16-March 8, 1980, in St. Louis. The comparison of the results on teflon and glass fiber filters for total carbon analyses by the GRALE technique and for elemental carbon by reflectance analysis during this period is shown in Figure 10. The results from both filters agree quite well (total carbon slope = 0.99 ± 0.09, r = 0.95, elemental carbon slope = 1.18 ± 0.26; r = 0.93). These data are summarized in Table 1.

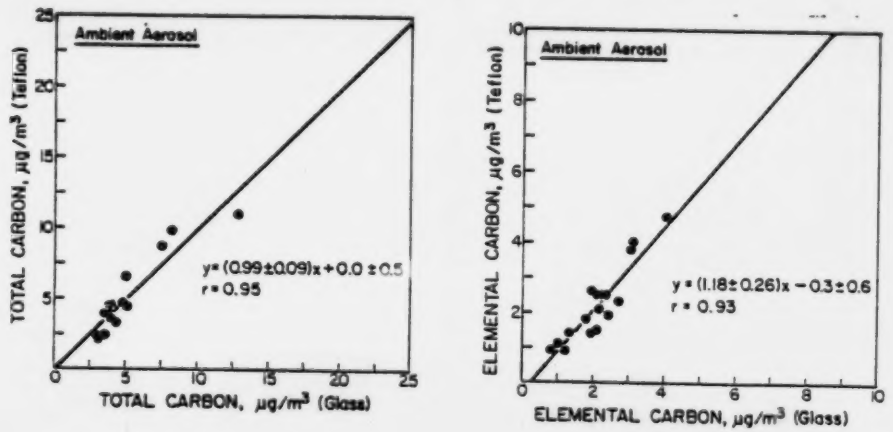


Figure 10. Comparisons of (a) total carbon analysis by the GRALE technique and (b) elemental carbon analysis by the reflectance method of atmospheric aerosols on teflon and glass fiber filters.

TABLE 1. AVERAGE AMBIENT AEROSOL CARBON CONCENTRATION MEASURED ON TEFLON AND GLASS FILTERS. SAMPLES WERE COLLECTED IN ST. LOUIS, MO DURING FEBRUARY AND MARCH, 1980

All values are $\mu g/m^3$

	Teflon Filters	Glass Fiber Filters
Total Carbon	5.5 ± 2.2	5.5 ± 2.7
Elemental Carbon	1.8 ± 1.1	2.0 ± 0.8
Mass (beta gauge)	---	22.1 ± 12.9

9. EMISSIONS AND AIR QUALITY RELATIONSHIPS FOR ATMOSPHERIC CARBON PARTICLES IN LOS ANGELES

An emission inventory for fine particle aerosol carbon has been constructed for the Metropolitan Los Angeles area and compared to the results of ambient sampling (Cass, Boone, and Macias, 1981). Information on the level of source activity, total aerosol emission rate, particle size and chemical composition was used to estimate the mass emission rate of particulate organic and elemental carbon in this urban area. It was found that carbonaceous particle emissions to the atmosphere arise from more than fifty classes of mobile and stationary air pollution sources. Emission data for elemental carbon at present contain significant uncertainties. Methods for verifying the consistency of carbonaceous aerosol emission inventories thus are important. Verification tests based on comparison of the ratio of organic carbon to elemental carbon and lead in source emissions versus that measured in the atmosphere were developed in this project. Using these tests, excellent agreement was found between the emission inventory and results of ambient sampling in Los Angeles during January and February 1980. The emission inventory results are shown in Figures 11 and 12.

Figure 11.

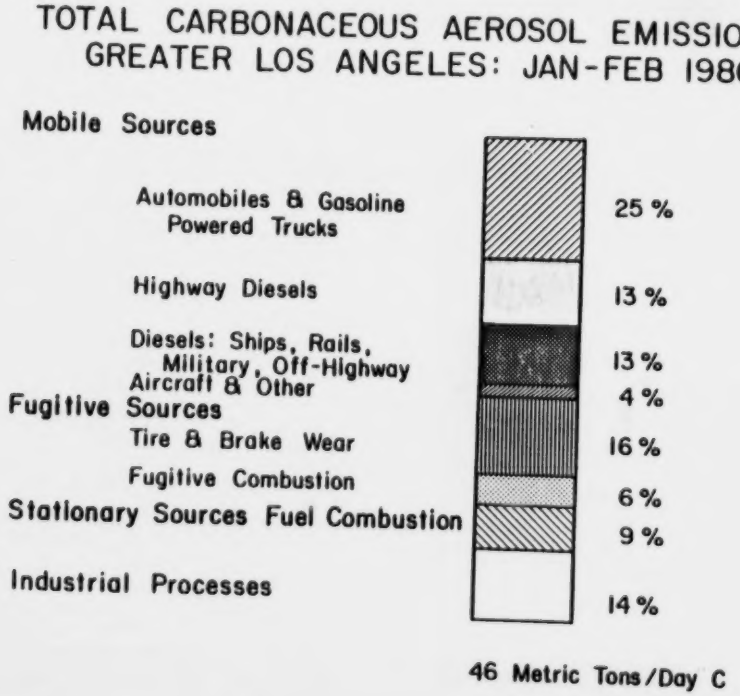
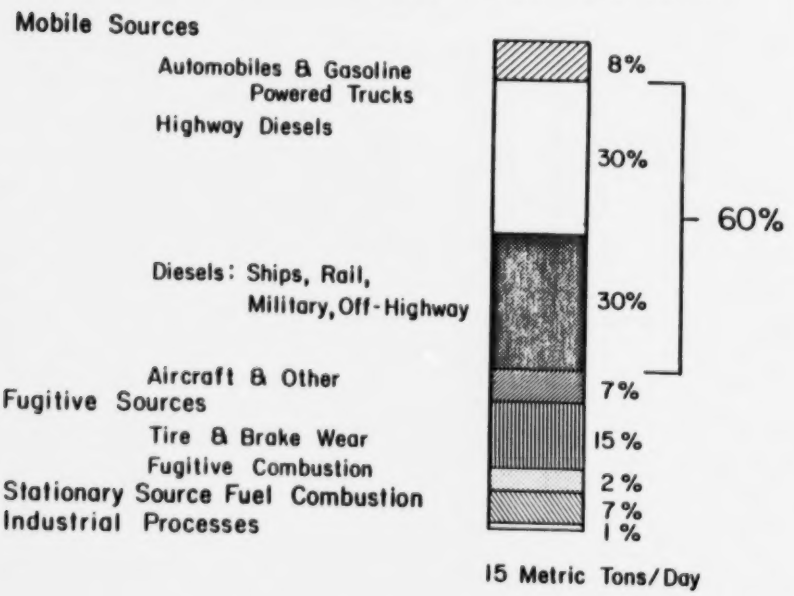


Figure 12.

SOURCES OF NON-VOLATILE CARBON
GREATER LOS ANGELES: JAN-FEB 1980



7. CARBONACEOUS URBAN AEROSOL -- PRIMARY OR SECONDARY?

The relative contribution of primary and secondary carbon to urban aerosol has been studied in this project (Chu and Macias, 1980). Some data from the ACHEX study in Los Angeles have been reexamined using new values for the carbon and lead emissions. Data on total carbon, elemental carbon and lead in fine particle samples collected in St. Louis were examined.

FINE AEROSOL MASS BALANCE

A mass balance for fine particle aerosol can be calculated from the carbon, sulfur, nitrogen, and mass concentration data with the assumptions that aerosol sulfur is in the form of sulfate, that nitrogen is in the form of ammonium ion, and that carbon exists either in the elemental form as soot or in organic compounds. The assumptions of nitrogen and sulfur chemical form are consistent with the N/S ratio determined for all samples as shown in Figure 13. The organic carbon is estimated from the difference between measurements of total carbon and elemental carbon multiplied by 1.5 (e.g. $-CH_2O_{1/4}-$). The fine particle mass balances calculated in this way for summer and winter sampling periods are shown in Figure 14. The average mass concentration was about the same in each sampling period ($\sim$39 $\mu g\ m^{-3}$) but several of the measured constituents, particularly elemental carbon, did not remain constant. However, we have evidence that leads us to think that these data can be used to determine the presence of secondary organic aerosol. For example, the ratio of organic carbon (OC) to elemental carbon (EC) is greater in the summer sampling period [OC/EC (summer) = 4.3, OC/EC (winter) = 1.8]. We contend that this increase is most likely due to an increase in secondary organic aerosol. This increase of elemental carbon in the winter, which may be due to increased space heating and wood burning, somewhat confounds our attempts to use elemental carbon as a tracer for all primary carbonaceous pollutants.

We have also looked for the presence of increased secondary organic aerosol by calculating the fine aerosol mass balance in both summer and winter during periods of high and low sulfate concentrations. Formation of secondary sulfate aerosol can cause elevated levels of sulfates and has been linked to periods of regional scale haziness in the eastern U.S. Our rationale for this analysis procedure is that during periods of increased concentration of secondary sulfate aerosol there might also be an increase in secondary carbon aerosol. The median sulfate cocnetration (8.4 $\mu g\ m^{-3}$) was chosen to separate the high and low sulfate concentration ranges. The average concentration and percentage of the fine mass for the measured constituents in the two concentration ranges are shown in Figure 15. In the high sulfate concentration regimes the absolute concentration of all measured species increased. However, the relative concentration of

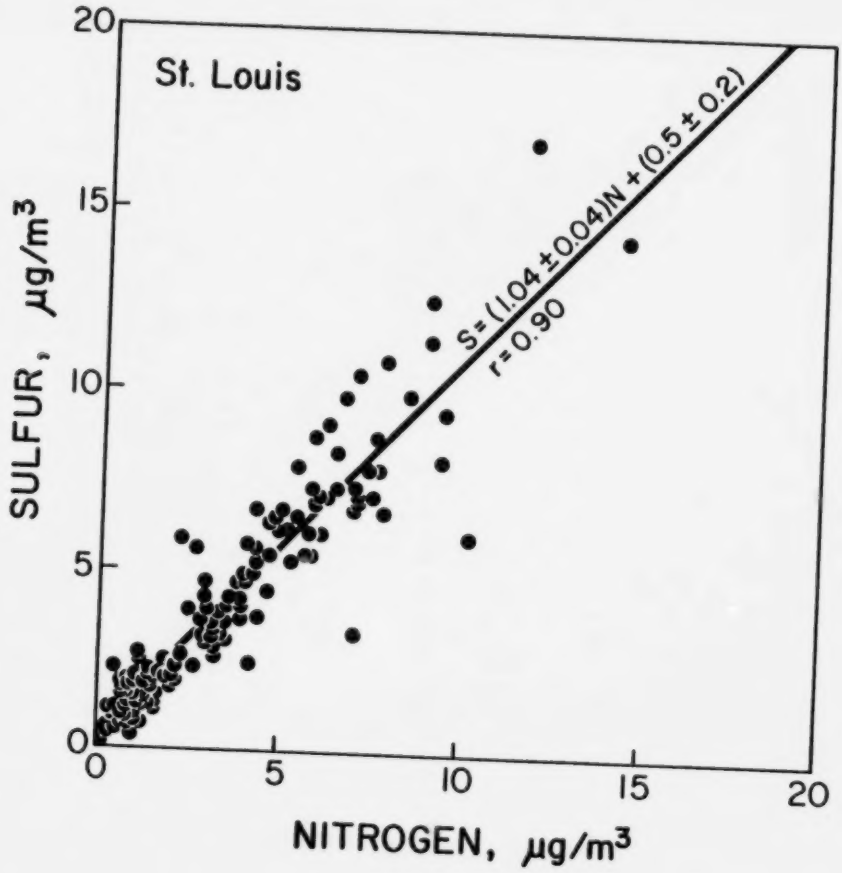


Figure 13. Scatter plot of aerosol sulfur and nitrogen concentrations for individual samples collected in St. Louis. The slope is within error of the stoichiometric ratio for $(NH_4)_2SO_4$.

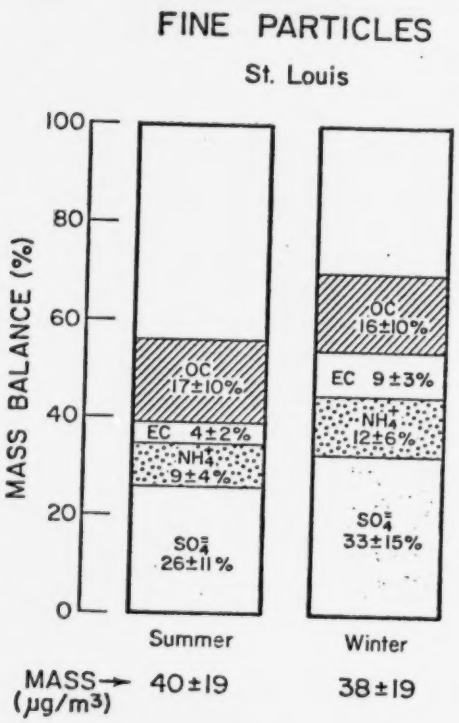


Figure 14. Mass balance of St. Louis fine aerosol broken down into summer and winter sampling periods.

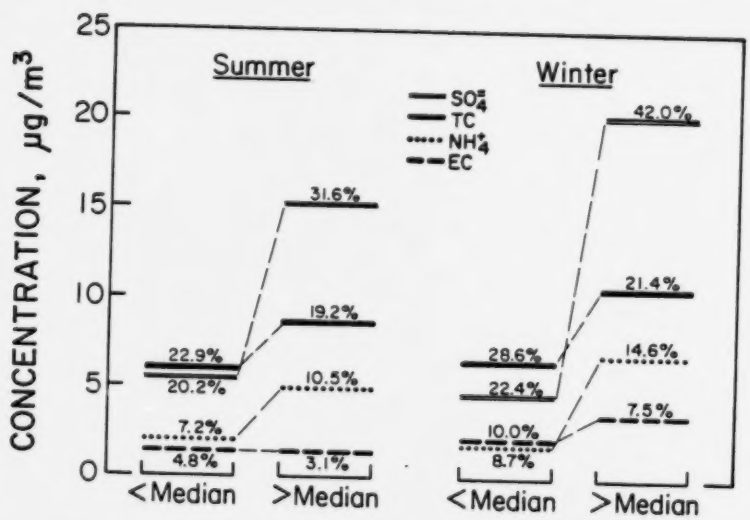


Figure 15. The mass balance of St. Louis fine aerosol divided into high and low sulfate concentration regimes for summer and winter. The median sulfate concentration of 8.4 $\mu g/m^3$ was used as the separation point for high and low sulfate regimes.

total and elemental carbon decreased. On the other hand the relative amounts of sulfate ion and ammonium ion increased in the high sulfate regime. The presence of secondary organic carbon aerosol is detectable in the high sulfate regime during the summer from the organic carbon to elemental carbon ratio [OC/EC (high sulfate, summer) = 5.2; OC/EC (low sulfate, summer) = 3.8]. However, in the winter sampling there was no detectable secondary organic carbon from this ratio [OC/EC (high and low sulfate, winter) = ∿1.9].

ELEMENTAL-TOTAL CARBON CORRELATIONS

The relationship between elemental carbon and total carbon in all samples is shown in Figure 16a. The data are scattered and not well correlated

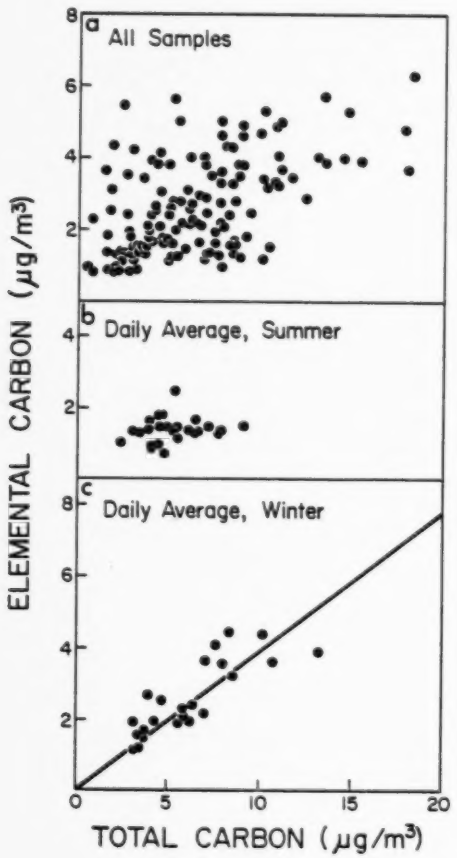


Figure 16. Plot of elemental carbon concentration versus total carbon concentration for particulate samples collected in St. Louis: (a) all samples (6-h); (b) 24-h averages for summer samples, (3) 24-h averages for winter samples.

(r = 0.63). This is different fom the results reported by Rosen et al. (1980); however, our data are 6-h samples while Rosen examined 24-h samples. In order to more accurately compare the two data sets we have averaged the 6-h samples to determine the 24-h average concentrations of elemental and total carbon for the summer and winter, respectively (Figure 16b and c). The winter data show a strong correlation (r = 0.86) in agreement with the previous work (Rosen et al., 1980); this correlation is not seen in the summer data (r = 0.14). We conclude from this that in the winter sampling period in St. Louis there is very little secondary organic aerosol present. What is there is covarying with the primary carbon aerosol. On either time scale in the summer there appears to be significant amounts of secondary carbon which vary independently of the primary carbon aerosol in St. Louis. This difference in the correlations on different time scales may also imply that diurnal patterns of primary and secondary carbon aerosol are different.

Automotive Tracers

The work of Cass, Boone and Macias (1981) indicates that in Los Angeles 90% of the elemental carbon aerosol and 71% of the primary total carbon aerosol is due to mobile sources. Although a complete carbonaceous aerosol emission inventory has not been carried out for St. Louis, it is reasonable to assume that mobile sources of carbonaceous aerosol are quite important in that airshed as well.

Automotive exhaust is by far the major source of particulate lead in urban atmospheres. In this study we found a strong correlation between lead and bromine (r = 0.91) during the winter of 1980, as shown in Figure 17a This is as expected for automobile emissions because the principal lead component in the exhaust is PbBrCl. The Br/Pb ratio of 0.16 is lower than the stoichiometric value of 0.39 due to the loss of Br from the aerosol with time. Thus, lead appears to be a good tracer for auto emission in the St. Louis aerosol. Interestingly, the elemental carbon and lead are well correlated (r = 0.84), as shown in Figure 17b and yet lead comes mainly from the combustion of leaded gasoline while the bulk of the elemental carbon comes from unleaded diesel fuel. The high correlation is most likely a result of the fairly constant mixture of leaded, unleaded, and diesel vehicles in the automotive traffic. Total carbon and lead are also well correlated (r = 0.82) as shown in Figure 17c during this winter period which agrees with the high correlation between elemental carbon and total carbon (Figure 17d). Thus during the winter period primary emissions from mobile sources seem to dominate the carbonaceous aerosol. The least squares fits to the data of total carbon and elemental carbon versus lead have positive intercepts which suggest the presence of a small but not negligible non-mobile source of these carbonaceous particles.

The carbon to lead ratios in St. Louis and Los Angeles on selected days are plotted as a function of time of day in Figure 15. Far more variation can be seen in the LA data although an increase in the C/Pb ratio in St. Louis is seen at midday on two days. The C/Pb ratio is also much lower in the St. Louis data. This supports the previous conclusion that primary carbon is dominant in St. Louis in the winter sampling period. It also suggests that more secondary carbon aerosol is present in LA than in St. Louis.

SUMMARY

Primary carbon particles dominate the carbonaceous aerosol under certain conditions while substantial secondary carbon may be present at other times. However, the importance of secondary carbon contributions is much less obvious when 24-h samples are examined. With shorter time averaged samples (e.g. 6-h or less) the increase in secondary carbon formation can be more easily detected. Secondary carbon appears to be more important in the summer rather than winter, in the afternoon rather than the early morning, and in LA rather than St. Louis. It should be noted that these conditions of increased secondary carbon aerosol formation are also more favorable conditions for photochemical reactions. Our detailed emission inventory for L.A. indicates that much more primary carbon exists in the urban aerosol than was thought previously. This is in agreement with the data. Our analysis shows that even on the very smoggy days in the ACHEX study there were times when primary carbon dominated the carbonaceous aerosol.

Finally, the use of aerosol lead and elemental carbon have been shown to be useful tracers for primary carbonaceous aerosol. If these data were combined with information on the detailed speciation of the organic carbon particles, a rather complete understanding of the carbonaceous aerosol would be possible.

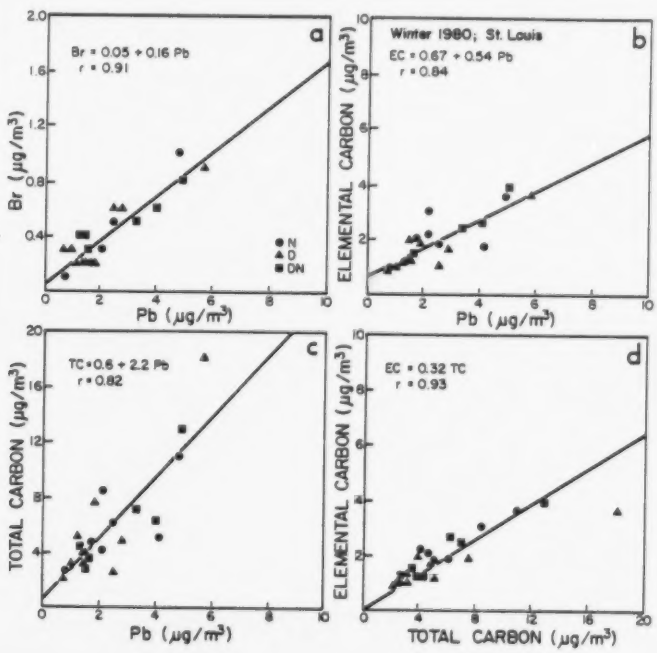


Figure 17. Plots of aerosol constitutents in St. Louis, winter 1980: (a) Br versus Pb; (b) elemental carbon versus Pb; (c) total carbon versus Pb; and (d) elemental carbon versus total carbon for particulate samples collected during the day (D), during the night (N) and from 3 PM to 9 PM (DN).

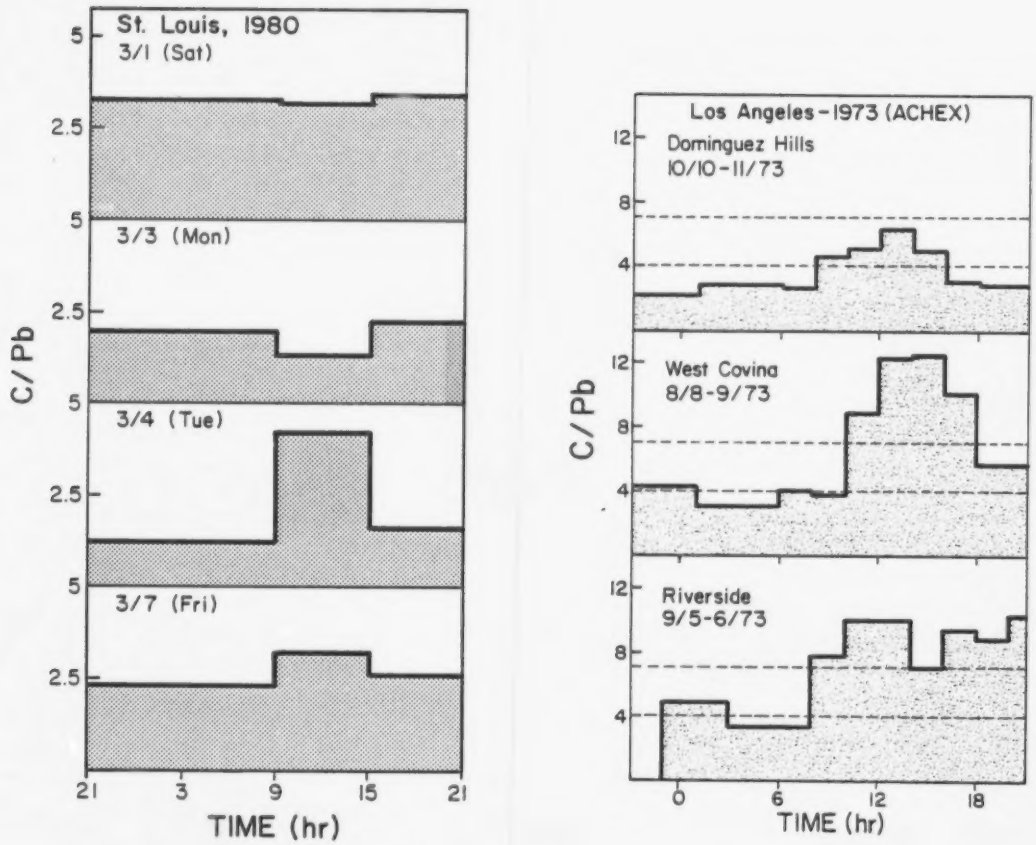


Figure 18. Plot of the aerosol C/Pb ratio as a function of time in Los Angeles and St. Louis.

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